

KINETICS AND MECHANISM OF CATALYTIC GASIFICATION OF COAL

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1. Introduction

In the recent years experiments for the gasification of German hard coal have been carried out using several alkaline compounds, especially K_2CO_3 , as catalysts. The work has been performed within the framework of the project "Prototype Plant Nuclear Process Heat" aiming at the use of heat from high temperature nuclear reactors (HTR) for the performance of the gasification. In this case the use of catalysts has special interest as the outlet temperature of the HTR is limited to about 950° /1,2/. Therefore, gasification temperature should be as low as possible (e.g. $750^\circ C$) to keep the temperature difference between the heat exchanger flown through by hot helium from the HTR and the reacting coal as high as possible. Special interest has been directed to kinetics and mechanism in order to get a basis for modelling of gasification reactors. In the following firstly experiments will be described which have been performed in laboratory scale. Then the effects of the catalysts in a big fluidized bed will be shown.

2. Order of Reaction with Respect to C and Related Reaction

Models

Carbon conversion during gasification of coal is particularly dependent on the C-concentration in the solid, on temperature, on total pressure and on the partial pressures of the gasifying agent and the products. Thus, it is generally described by complex equations for the reaction rates assuming a Langmuir-Hinshelwood mechanism. For steam gasification at low partial pressures of the products H_2 and CO and at constant partial pressure of the steam reaction rates r can be described much more simple as it is only a function of the C-concentration of the solid and the temperature as follows:

$$r = k_o \exp (- E/RT) c^n \quad 1)$$

with n : order of the reaction with respect to C

k_o : frequency factor

E : activation energy

c : C-concentration.

For the uncatalyzed reaction values of n have been found between $2/3$ and 1 . Then r can be expressed as

$$r_s = \frac{dx}{dt} \frac{1}{(1-x)^{2/3}} \quad \text{for } n = 2/3 \text{ or} \quad 2)$$

$$r'' = \frac{dx}{dt} \frac{1}{1-x} \quad \text{for } n = 1 \quad 3)$$

with X = carbon conversion.

For coal gasification catalyzed with alkaline compounds Mims and Pabst /3/ have reported that n can be 0 at low degree of carbon conversion and will change to $n = 1$ and beyond at higher degrees of conversion corresponding to

$$r' = \frac{dx}{dt} \quad \text{for } n = 0. \quad 4)$$

The existence of different values for n can be explained as follows: If all C-atoms are equally accessible and active during the course of the gasification reactions between C and H_2O then the assumption of $n = 1$ makes sense. However, in a more detailed consideration it has to be taken into account that the different C-atoms may show different activities to gasification and that the reaction will occur at the internal surface of the porous solid. Both effects are complex and not predictable by a simple theory. The reaction order of $n = 2/3$ can be deduced on the basis of a geometric pore model if the effects of crystalline structure of the C-matrix are neglected. For catalyzed gasification it can be assumed that the C-atoms in the neighborhood of catalytically active particles show a much higher reaction activity. Consequently, they are preferably consumed. The reaction order will then be a function of the accessibility of these "catalyzed C-atoms" during the course of conversion. Provided that the catalyst atoms are mobile, the concentration of the C-atoms has no influence, and the reaction order will be 0.

3. Experimental Results Concerning the Reaction Order and the Influence of the Catalyst Concentration

First of all the reaction order for the uncatalyzed gasification of a char shall be discussed. Fig. 1 shows as an example the measured reaction rates r_s and r'' plotted against the degree of gasification assuming a reaction order of $2/3$ or 1 , respectively /4/. The reaction rate r_s remains constant for a degree of conversion ranging between 20 and 70 % and decreases rapidly beyond 70 %. That means that the assumption of $n = 2/3$ gives the best fit for the experimental values for this char. In other experiments, however, reaction orders closer to 1 than $2/3$ have been determined.

A reaction order of $2/3$ has been found for the catalytic gasification, too, adding 0.56 to 5.1 % K to a low ash char made from the coal Westerholt, as can be seen by fig. 2 /5/. The mode of char preparation is also given in /5/. It can be stated that r_s remains constant in a wider range of C-conversion (burn-off) as compared with the uncatalyzed case (fig. 1). It follows that the K-atoms are excellently distributed in the char and that the C-atoms in the neighborhood of the catalysts are equally well accessible by the steam during the course of burn-off.

As these experiments are carried out at 700°C a free mobility of the catalyst cannot be expected as will be shown later on. A detailed analysis of the results leads to the following equation for the description of the rate of the catalyzed reaction r_s dependent on X and the K -concentration c_K :

$$r_s = \frac{dx}{dt} \cdot \frac{1}{(1 - X)^{2/3}} = (k_1 + k_2 c_K) \quad (5)$$

$$k_1 = 0,00276 \frac{1}{\text{min}}$$

$$k_2 = 0,00953 \frac{1}{\text{min} \cdot \text{wt}\%K}$$

As it is shown in fig. 3 the rate r_s increases linear with the K -concentration c_K in the sample.

Different results have been found at gasification temperatures of 880°C and a pressure of 1 bar with coal "Lohberg" (35.7 % v.m. m.a.f., 5.3 % ash m.f.) /6,7/ using different alkaline compounds. In fig. 4 reaction rates r' are plotted depending on the degree of conversion assuming a reaction order $n = 0$. This assumption is confirmed by the horizontal slope of the curve for carbon conversions up to 90 %. This deviation from the findings given in fig. 2 may be explained by the assumption that the catalyst is free mobile at this higher temperature as will be discussed later.

Fig. 5 demonstrates the different effects of equal alkali concentrations (in mole/g coal) for the different alkali group elements. For each alkali metal there is a concentration range in which the zero-order reaction rate r' increases nearly proportionally to the catalyst concentration. The slope of this straight line is increasing with increasing atomic number of the alkaline metals. It is remarkable that the boiling point of the metals decreases in the same order (table 1). As will be discussed later, our experiments have shown that the alkaline carbonates are reduced to the metals by the carbon while heated up to reaction temperature. The metals are bound to the C-atoms by a mechanism which is not yet clear. Obviously, the effectiveness of these metals is strongly related to their mobility on the surface and the latter surely depends on the boiling point relative to the reaction temperature. As shown in table 1 the boiling

Table 1: Boiling Point of Alkaline Metals

Metal	Atomic Number	Boiling Point °C
Cs	55	690
K	19	760
Na	11	892
Li	3	1330

temperatures of Cs and K are lower than the reaction temperature of 880°C (fig. 5). In this case a high mobility of both metals results in a high catalytic effectiveness. The boiling temperature of Na is beyond, that of Li is far beyond 880°C with the effect that the catalytic activity is decreasing in this order. Furthermore, our experiments have shown that Li probably is present as oxide instead of metal.

4. Desactivation of the Alkali by Mineral Matter

It can already be seen from fig. 5 that low concentrations of catalyst lead to no increase of the reaction rate. As has been confirmed by detailed studies this observation can be explained by reactions of alkali with clay minerals in the coal which lower the catalytic activity. Relevant results are shown in fig. 6 whereby different concentrations of K_2CO_3 have been added to chars of ash content between 6 and 30 %.

For the 6.6 % ash char the catalytic effects are observed after 3 % K_2CO_3 have been added. The rates then increase proportional to the concentration. For the 18.8 % ash char catalytic gasification starts distinctly with a minimum of 7.5 % K_2CO_3 addition and in the case of the 13 % ash char approximately 12.5 % K_2CO_3 seem to be necessary. From the shape of the curve depending on burn-off it can be derived that $n = 2/3$ is valid to some extent for the char with a relatively low ash content. For the chars containing a higher amount of mineral matter the reaction rates decrease systematically with burn-off whereby different slopes have been measured in the different ranges of burn-off. It can be concluded that rapid and slow reactions of desactivation take place, as the alkali reacts with different components of the mineral matter. Active in consuming alkali have been proven to be the clay minerals kaolinite and illite and kaliophilite is found as a product of the reaction of both clay minerals with potassium carbonate /8/.

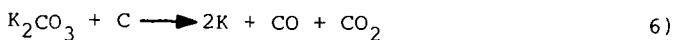
5. Activation Energy and Frequency Factor

Investigating the kinetics of catalytic gasification, special attention has to be paid to the temperature region in which chemical reaction is rate determining. In this region catalysts are expected to have maximum effect. However, in consequence of the reaction rate increase the transition temperature between the chemical viz. diffusion controlled regions should change to lower values. This effect has been verified experimentally. In the Arrhenius-type diagram (fig. 7) the transition temperature can be located at 700°C, whereas for the uncatalyzed gasification no transition is to be observed up to 850°C.

The investigations described below are therefore restricted to the domain of chemical reaction controlled gasification rate. As shown in fig. 8 increasing amounts of potassium shift the lines in the Arrhenius diagram without changing the slope /6,7/, i.e. the activation energy is nearly unaffected by the catalyst while the frequency factor increases proportional to the amount of potassium added. In the case of Na-catalyzed gasification, results were similar besides the fact that the uncatalyzed reaction exhibits an activation energy slightly different from those found in the experiments with distinct Na-concentrations.

6. Chemical State of the Alkali Catalysts and Mechanism

Thermogravimetric analyses were performed to examine the decomposition reaction of K_2CO_3 on the surface of char and the evaporation of elemental potassium from a char-potassium-mixture /6,7/. It can be concluded that the first reaction step is the reduction to elemental potassium by the carbon:

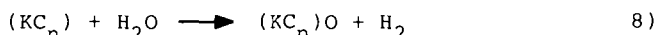


The potassium has been found to undergo a relatively strong bonding to the carbon. This is indicated by an extremely small evaporation rate of potassium metal in the presence of carbon. Thus the conclusion seems to be justified that the second step consists in the formation of a potassium-carbon-complex KC_n :

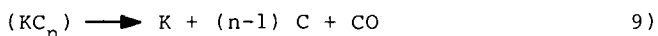


The value of n is approximately 5.5 which results from our evaporation experiments. The exact status of the bonding between alkaline metal and the carbon is not yet understood, however, we assume that there is a bonding by an electron transfer from the K-metal to the C-atom. Other authors stress the possibility of a bonding between carbon-oxygen complexes and the K-metal /9/.

The next reaction steps are speculative. The assumption seems reasonable that in a third step K-C-complexes are converted to surface oxides and hydrogen by the steam:



The fourth step should be the desorption of the surface oxide as CO thereby restoring the metallic state of the potassium:



Migration of potassium may form a K-C-complex again because potassium is mobile - at least at temperatures of 800 to 880°C thus repeating step 2 (equation 7) and completing the reaction cycle. In parallel to the gasification the desactivating reactions with coal minerals mentioned above occur. In addition potassium may be deactivated by re-establishing the potassium oxide or carbonate by reactions with steam or product gases. At high degrees of C-conversion the oxides or salts may form larger crystallites because of the high K-concentrations. Potassium then loses contact to the carbon atoms and reduction into the metal is no longer possible. This results in a severe desactivation. As to be seen in fig. 2, 4, and 6 such a desactivation occurs at C-conversions beyond 80 or 90 %.

7. Experiments on Larger Scale

On the basis of results of exploratory research in the laboratory a number of runs have been performed in a semi-technical plant with a fluidized bed of about 4 m³ volume heated by an immersed helium-flow heat exchanger /10/. K_2CO_3 and other active substances have been fed along with the coal in a dry mixture into the gasifier. Fig. 9 summarizes the reaction rates for an anthracite, a high volatile bituminous coal without catalyst and doped with different amounts of K_2CO_3 . For high volatile bituminous coal an increase of the reaction rate compared to anthracite by a factor of 2.5 can be stated. A doping with 2 or 3 % K_2CO_3 to the latter has a relatively modest effect. This can be explained by side reactions of K_2CO_3 with mineral compounds in the coal ash with the consequence of loss of catalytic activity. However, if 4 % K_2CO_3 are added a steep increase

of reaction rate by a factor of about 20 can be achieved. As has been predicted theoretically, the mean fluidized bed temperature decreases to 740°C. A steam decomposition of 30 % at a coal feed rate of 400 kg/h and an average carbon conversion of 37 % (in the fully back-mixed system) have been measured.

7. Discussion

Steam gasification catalyzed by potassium has been found to follow a varying reaction order with respect to carbon depending on the kind of char, ash content, and temperature. For the gasification of low-ash char, deviations of zero-order is ascribed to a restricted mobility of the catalyst, as it is found to occur especially at low temperatures, whereas mineral matter change the amount of active catalyst during gasification and thus produces apparent reaction orders that can even exceed $n = 1$. Chemical state of the catalyst on char under inert conditions has been found to be rather metallic than oxidic, but a bonding to carbon has been proven. Concerning reaction mechanism, the principle of catalytic action seems to be not a reaction path with a lower activation energy than for uncatalyzed reaction but an increase in the number of active sites. In this aspect, the mechanism of alkali catalysis is like that of earth alkali catalysis for which Otto et al /11/ reported a constant activation energy and an increased frequency factor.

Literature

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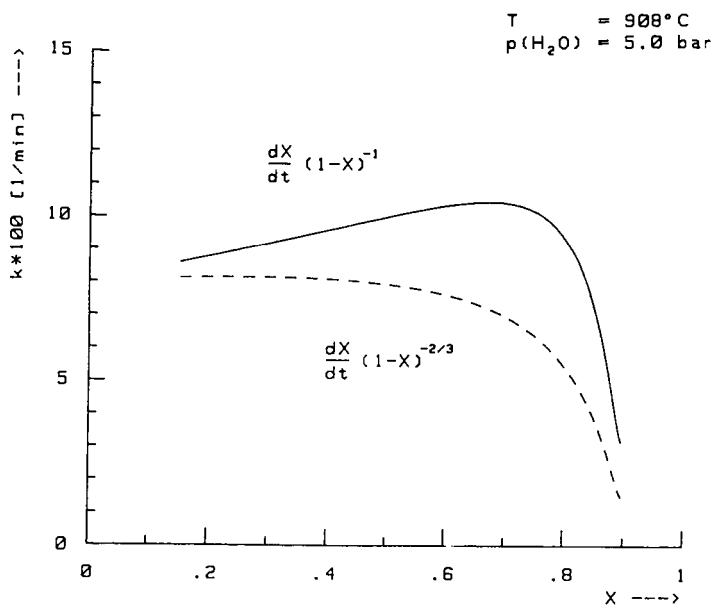


Fig. 1: Comparison of 1st-order and 2/3rd-order-reaction rate of a steam gasification run

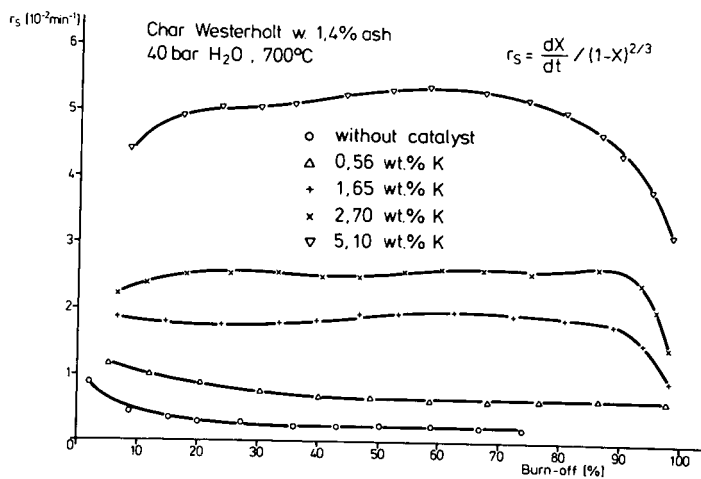


Fig. 2: Reaction rate based on order 2/3 for catalytic gasification of a low-ash char

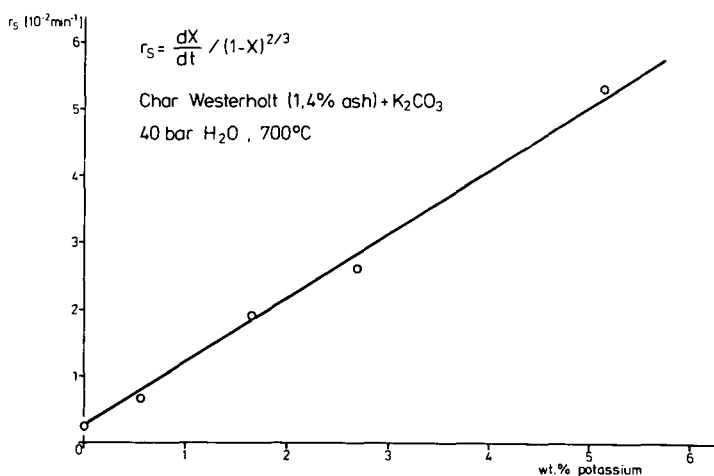


Fig. 3: Correlation of reaction rate r_s with potassium concentration for steam gasification of a low-ash char

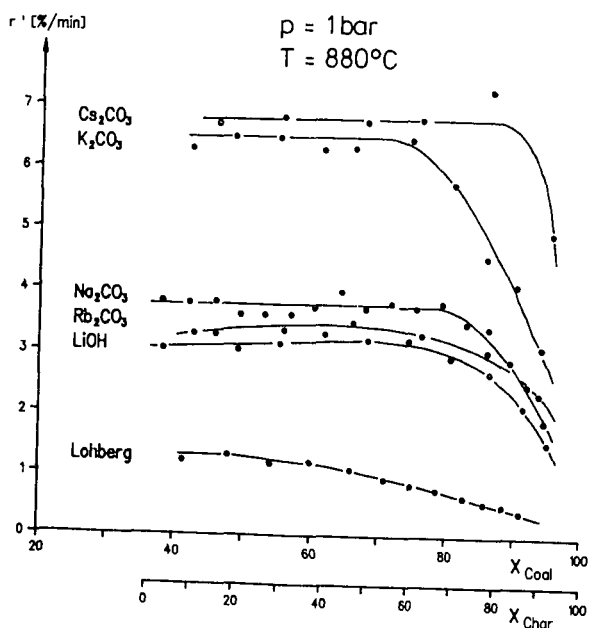


Fig. 4: Steam gasification of "Lohberg" coal with alkali catalysts as a function of C-conversion

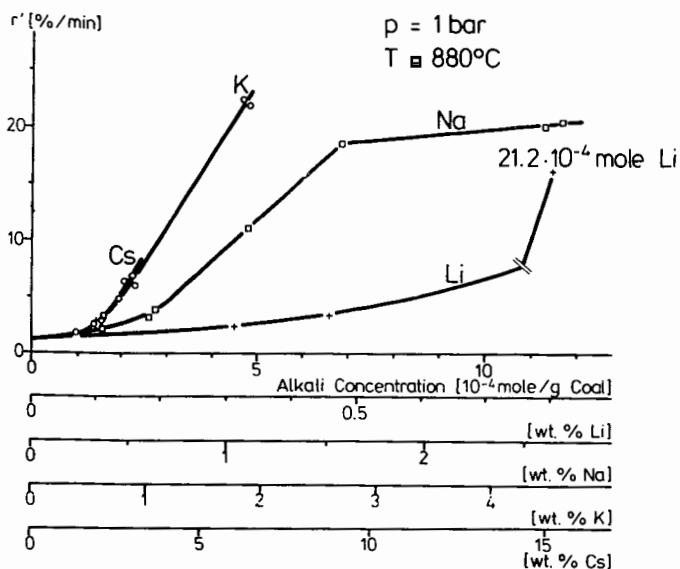


Fig. 5: Concentration dependance of steam gasification of coal "Lohberg" with different group elements

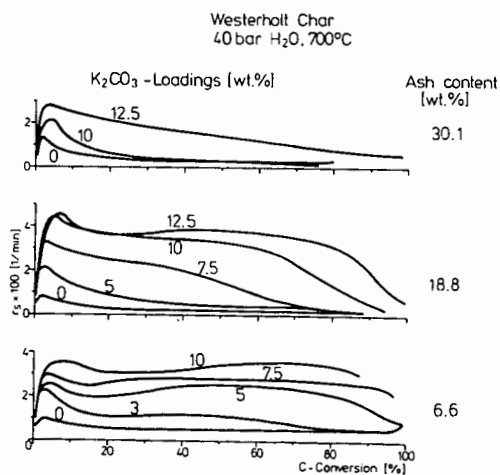


Fig. 6: Catalytic steam gasification of Westerholt char with different potassium and ash contents - evaluated assuming reaction order $n = 2/3$ -

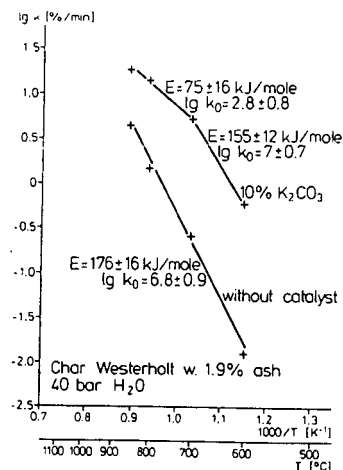


Fig. 7: Activation energy for non-catalytic and potassium-catalyzed steam gasification

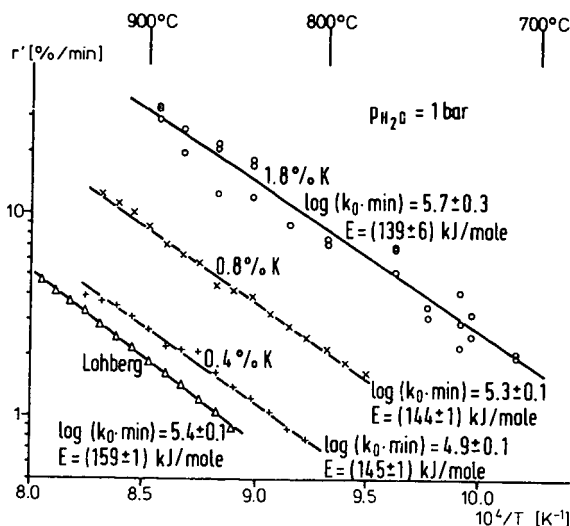


Fig. 8: Activation energy and frequency factor as function of potassium catalyst for the gasification of "Lohberg" coal

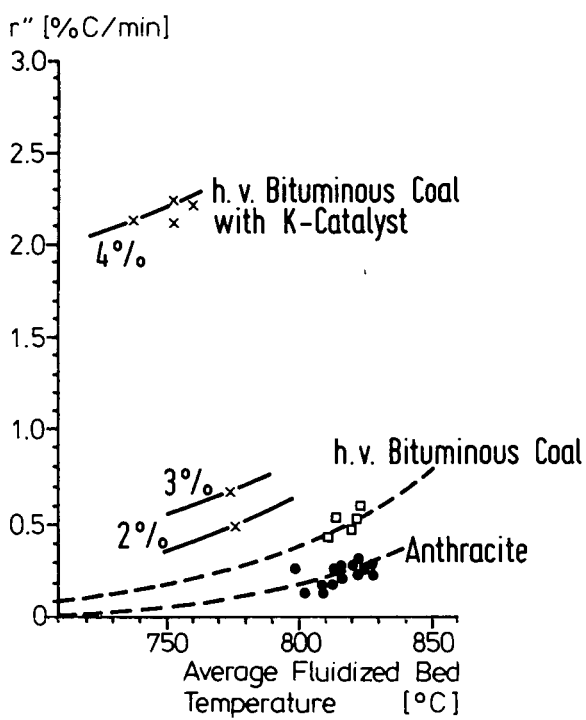


Fig. 9: Rates of catalyzed and uncatalyzed gasification in a fluidized bed reactor (height 4 m, pressure 40 bar) - The weight percent of K_2CO_3 added is noted at the curves